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Climate extremes dominating seasonal and interannual variations in carbon export from the Mississippi River Basin

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Abstract Knowledge about the annual and seasonal patterns of organic and inorganic carbon (C) exports from the major rivers of the world to the coastal ocean is essential for our understanding and potential management of the global C budget so as to limit anthropogenic modification of global climate. Unfortunately our predictive understanding of what controls the timing, magnitude, and quality of C export is still rudimentary. Here we use a process-based coupled hydrologic/ecosystem biogeochemistry model (the Dynamic Land Ecosystem Model) to examine how climate variability and extreme events, changing land use, and atmospheric chemistry have affected the annual and seasonal patterns of C exports from the Mississippi River basin to the Gulf of Mexico. Our process-based simulations estimate that the average annual exports of dissolved organic C (DOC), particulate organic C (POC), and dissolved inorganic C (DIC) in the 2000s were $2.6 \pm 0.4\,\mathrm{Tg\,C\,yr^{-1}}$, $3.4 \pm 0.3\,\mathrm{Tg\,C\,yr^{-1}}$, and $18.8 \pm 3.4\,\mathrm{Tg\,C\,yr^{-1}}$, respectively. Although land use change was the most important agent of change in C export over the past century, climate variability and extreme events (such as flooding and drought) were primarily responsible for seasonal and interannual variations in C export from the basin. The maximum seasonal export of DIC occurred in summer while for DOC and POC the maximum occurred in winter. Relative to the 10 year average (2001–2010), our modeling analysis indicates that the years of maximal and minimal C export cooccurred with wet and dry years (2008: 32% above average and 2006: 32% below average). Given Intergovernmental Panel on Climate Change-predicted changes in climate variability and the severity of rain events and droughts of wet and dry years for the remainder of the 21st century, our modeling results suggest major changes in the riverine link between the terrestrial and oceanic realms, which are likely to have a major impact on C delivery to the coastal ocean.

1. Introduction

Carbon (C) transport by rivers plays an integral role in both terrestrial and aquatic ecosystem processes, serving as a critical pathway in the global carbon cycle [*Butman and Raymond*, 2011; *Cole et al.*, 2007; *Raymond et al.*, 2013]. Inorganic and organic forms of C include dissolved inorganic C (DIC), dissolved organic C (DOC), and particulate organic C (POC), and these various forms of C support basic aquatic food web processes, provide important protection against harmful ultraviolet radiation, and have a profound influence on chemical properties in aquatic environments [*Findlay*, 2010; *Raymond and Cole*, 2003; *Tank et al.*, 2010]. Riverine C fluxes also play an important role in the overall C budget of the ocean [*Bauer et al.*, 2013; *Cole et al.*, 2007]. Environmental and ecological consequences of riverine C fluxes are dependent on both the total amount and relative proportions of different chemical forms of C [*Dhillon and Inamdar*, 2013]. While the general magnitudes of C export from the major rivers of the world are known, the relative magnitudes of the various forms of C, the long and short-term variations of the fluxes, and the underlying mechanisms controlling such variability remain largely uncertain. More precise quantification of the forms of organic and inorganic C exports to the coastal ocean and the factors

that influence them will enhance our understanding of the global C budget and also provide insights into the sustainability of the coastal ecosystems subject to changing climate and human impacts.

The Mississippi River basin is the third largest river basin and contains one of the most productive agricultural regions in the world [*Foley et al.*, 2004]. Over the past century, the Mississippi River basin has experienced profound land cover and land use change (LCLUC), driven largely by an unprecedented increase in food demand associated with a rapidly growing U.S. and global human population, and further development is likely in the coming decades [*Chen et al.*, 2006; *Mackenzie et al.*, 2000]. These changes have greatly influenced the magnitude, seasonal and annual variations of fresh water discharge, and associated C and nutrient exports from land to the Gulf of Mexico; this has resulted in enhanced productivity and altered biogeochemical cycles in the shelf ecosystem [*Donner et al.*, 2004; *Lohrenz et al.*, 1997, 1999; *Schilling et al.*, 2010] with potential negative consequences such as increasing severity of hypoxia [*Rabalais et al.*, 2002] and enhanced ocean acidification [*Cai*, 2011]. To develop effective strategies for sustainable management across the land-sea interfaces and reduce unintended negative consequences of human actions, it is necessary to enhance our predictive understanding of changes in watershed export brought about by both natural and anthropogenic changes on land. To date, most existing studies in this region have focused on either terrestrial or aquatic ecosystems separately or with greatly simplified linkages between them. A comprehensive characterization is lacking of the temporal and spatial patterns of riverine organic and inorganic C fluxes (DIC, POC, and DOC) and their responses to major changes in land use and management and climate change over the entire Mississippi River basin at seasonal, annual, and decadal time scales.

Recent synthesis studies indicate that human activities have caused a large increase in C flux from land to ocean since preindustrial times [*Bauer et al.*, 2013; *Regnier et al.*, 1997]. However, much uncertainty exists in understanding how climate extremes and variability at seasonal, annual, and decadal scales have affected the movement of water and C through terrestrial systems, watersheds and reservoirs, and major rivers to the ocean. Here we use the Dynamic Land Ecosystem Model (DLEM 2.0) [*Liu et al.*, 2013; *Tian et al.*, 2015] to investigate the short-term spatial and temporal patterns of carbon export from the Mississippi River basin to the Gulf of Mexico, focusing on the 2001–2010 interval. We use this mechanistic model to "experimentally" evaluate the relative contributions of major natural and anthropogenic factors to variability in carbon export. This integrated approach provides an example that can be applied to other terrestrial and river ecosystems to better understand and manage impacts of changes in climate, atmospheric chemistry, and land use on C fluxes across land-ocean interfaces.

2. Methods and Data

2.1. Model Description

The DLEM is a process-based land model which couples biophysical characteristics, plant physiological processes, hydrological and biogeochemical cycles, and vegetation dynamics and land use, to make daily, spatially-explicit estimates of carbon, nitrogen, and water fluxes and pool sizes in terrestrial ecosystems and inland waters [*Tian et al.*, 2012]. The DLEM 2.0 represents an improvement over previous versions of this model, especially in simulating water, carbon, and nutrient fluxes at the land-sea interface, where rivers enter the ocean (Figure 1) [*Liu et al.*, 2013; *Tao et al.*, 2014; *Yang et al.*, 2015; *Tian et al.*, 2015; *Ren et al.*, 2015]. Three major processes are involved to simulate the export of water, carbon, and nutrient including (1) generation of runoff and carbon leachates; (2) leaching of water, carbon, and nutrients from land to river networks; and (3) transport of riverine materials along river channels from upstream areas to coastal regions.

The hydrological module in the DLEM adopts a grid cell-based and single-column land-surface flow routing method [*Liu et al.*, 2013]. Water pools in each grid cell include lakes, streams, snowpack, and intercepted water by the vegetation canopy. The time step for simulating water flow from land to river and other water pools in the model is 30 min. The rate of water movement to the downstream grid cell is calculated based on water residence time of surface water [*Coe*, 2000]. The residence time of water in the river is calculated based on the length of the stream channel and the flow rate in each grid cell [*Coe*, 2000]. The residence time of water in lakes is assumed to be 10 times the river water residence time of the same grid cell. The transpiration is the area-weighted sum of all plant functional types (PFTs). Transpiration is simulated with the Penman-Monteith approach [*Wigmosta et al.*, 1994]. The maximum transpiration is set as the available soil water. Stomatal conductance is regulated by solar radiation, temperature, vapor pressure deficit, soil water
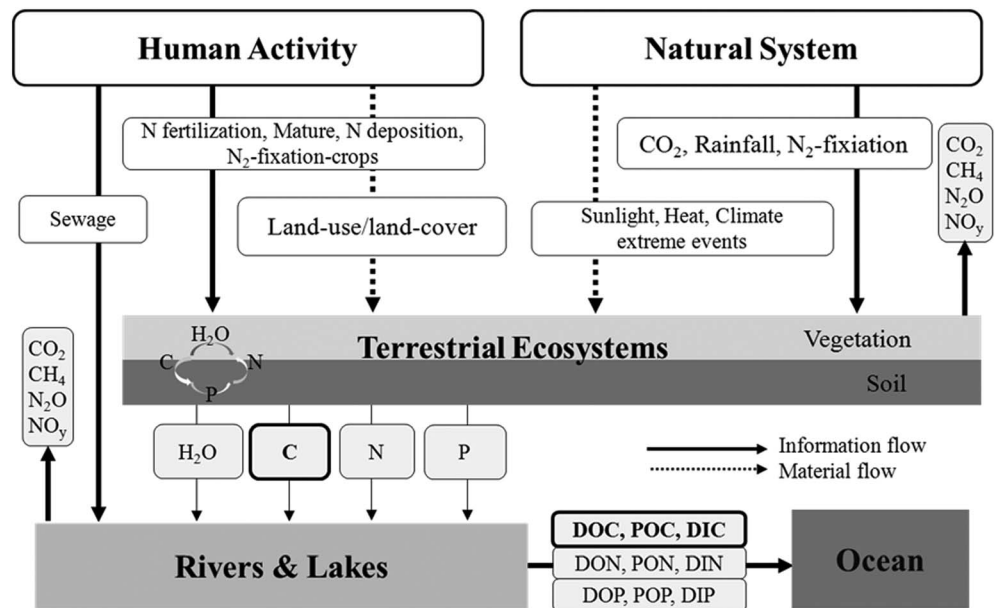
Figure 1. The modeling framework of carbon and nutrient fluxes at the land-ocean interface within the Dynamic Land Ecosystem Model (DLEM).

potential, and atmospheric CO_2 concentration [*Jarvis and Morrison*, 1981; *Chen et al.*, 2005; *Running and Coughlan*, 1988]. The equations for bare ground evaporation used by the Food and Agriculture Organization were adopted and improved in DLEM 2.0 [*Allen et al.*, 1998] by considering canopy effects on net radiation and aerodynamic resistance [*Belmans et al.*, 1983]. Additional details regarding hydrological processes in DLEM 2.0 can be found in our recent work [*Liu et al.*, 2013; *Tao et al.*, 2014; *Tian et al.*, 2014; *Yang et al.*, 2014a, 2014b].

Carbon transport along river channels is controlled by water movement from upstream grid cells to downstream grid cells. Details regarding model representation of carbon processes at the land-aquatic interface in DLEM 2.0 have been reported recently [*Tian et al.*, 2015]. Here we provide a brief description of the model simulations of carbon leachate production and in-stream transformations involved in carbon export.

2.1.1. Carbon Export From Soil to Streams

In DLEM 2.0, litter and soil organic matter are the sources of DOC leachate [*Chantigny*, 2003]. Production and subsequent export of DOC are simulated with the following equations:

$$R_{lchdoc} = SDOC \times fflow \times \frac{DOCC}{DOCC + lchb_{doc}} \tag{1}$$

where R_{lchdoc} is the export rate of dissolved organic carbon ($g\,C\,m^{-2}\,d^{-1}$), SDOC is the total amount of dissolved organic carbon in soil ($g\,C\,m^{-2}\,d^{-1}$), fflow is the runoff coefficient for export, DOCC is the concentration of dissolved organic carbon ($g\,C\,g\,soil^{-1}\,d^{-1}$), and $lchb_{doc}$ is the soil desorption coefficient for DOC ($g\,C\,g\,soil^{-1}\,d^{-1}$).

Export of POC is assumed to occur with soil erosion. In the DLEM 2.0, the soil erosion rate is calculated with the Modified Universal Soil Loss Equation [*Chaubey et al.*, 2007; *Williams and Berndt*, 1977]:

$$R_{lchpoc} = T_{occ} \times R_{erosion} \tag{2}$$

where R_{lchpoc} is the rate of particulate organic carbon production in conjunction with soil erosion ($g\,C\,m^{-2}\,d^{-1}$), T_{occ} is the concentration of total organic carbon in soil column ($g\,C\,g\,soil^{-1}$), and $R_{erosion}$ is the soil erosion rate ($g\,soil\,m^{-2}\,d^{-1}$).

Export of DIC in the DLEM 2.0 includes three processes: dissolution of atmospheric CO_2, dissolution of soil CO_2, and carbonate rock weathering. We assume that dissolution of atmospheric CO_2 to be the primary source of DIC in surface runoff, and we simulate this process according to Henry's law. Carbon dioxide dissolution includes two reactions. The first reaction is the process in which free CO_2 enters water and becomes

dissolved CO_2 and H_2CO_3, which collectively are referred to as $H_2CO_3^*$ that further dissociates to HCO_3^- and H^+. The amount of dissolved CO_2 is calculated with the following equations:

$$[H_2CO_3^*] = K_h * PCO_2 \tag{3}$$

where the brackets indicate concentration (M), PCO_2 is the partial pressure of atmospheric CO_2 (atm), and K_h is the Henry's law equilibrium coefficient (M/atm).

Another important source of DIC is soil carbonate weathering. We applied the following equations to account for this process [*Holford and Mattingly*, 1975; *Plummer et al.*, 1978]:

$$WR_{co3} = R_{co3} \times S_{area} \tag{4}$$

where WR_{co3} is the weathering rate of soil carbonate rock ($g\,C\,m^{-2}\,s^{-1}$), R_{co3} is the specific weathering rate of per unit area of carbonate rock ($g\,C\,m^{-2}\,s^{-1}$), and S_{area} is the surface area ratio of carbonate rock in the soil (m^2 carbonate m^{-2} soil).

2.1.2. In-stream Processes

Transformations of organic and inorganic carbon occur as they are transported through streams and lakes. Major in-stream processes considered in DLEM 2.0 include respiration of DOC and POC, deposition of POC, and outgassing of DIC.

We applied a first-order model to simulate DOC decomposition in streams and lakes in DLEM 2.0:

$$R_{doc} = DOC_{ls} \times K_{doc} \times (Q10)^{\frac{T-T_s}{10}} \tag{5}$$

where R_{doc} is the degradation rate of DOC in lakes or streams ($g\,C\,d^{-1}$), DOC_{ls} is the amount of dissolved organic carbon in lakes or streams in each grid cell ($g\,C$), K_{doc} is the calibrated value to represent the long-term average decomposition rate in lake and rivers ($0.01\,day^{-1}$), $Q10$ is the temperature coefficient of DOC decomposition in water bodies (2.0), T is the water temperature (°C), and T_s is the reference temperature (20°C).

Similarly, decomposition of particulate organic carbon is simulated as

$$R_{poc} = POC_{ls} \times K_{poc} \times (Q10)^{\frac{T-T_s}{10}} \tag{6}$$

where R_{poc} is the degradation rate of POC in water bodies ($g\,C\,d^{-1}$), POC_{ls} is the amount of particulate organic carbon in lakes or streams in each grid cell (g C), K_{poc} is the calibrated value to represent the long-term average decomposition rate in lake and rivers ($0.005\,day^{-1}$), $Q10$ is the temperature coefficient of DOC decomposition (2.0), T is the water temperature, and T_s is the reference temperature (20°C).

As flow rate decreases, POC is deposited with sediment in rivers and lakes. Under low-flow conditions, suspended POC leaves water bodies and accumulates in river bed or lake bed [*Merritt et al.*, 2003]. In DLEM 2.0, we simulate POC deposition with following equations:

$$POC_{dep} = W \times (POCC - POCC_{max}) \tag{7}$$

where POC_{dep} is the total amount of particulate organic carbon in water bodies (g C), W is the total water of rivers or lakes ($m^3\,d^{-1}$), POCC is the concentration of POC in rivers or lakes ($g\,C\,m^{-3}$), and $POCC_{max}$ is the POC holding capacity of water bodies ($g\,C\,m^{-3}$).

A considerable amount of DIC leaves streams and lakes in the form of CO_2. In DLEM 2.0, degassing is mainly driven by temperature, air CO_2 concentration, streamflow, and temperature [*Butman and Raymond*, 2011; *Guérin et al.*, 2007]:

$$DIC_{deg} = K_{deg} \times (W_{pco2} - SaW_{pco2}) \times 12 \tag{8}$$

where DIC_{deg} is the degasing rate in surface water bodies ($g\,C\,m^{-2}\,d^{-1}$), K_{deg} is CO_2 transfer velocity ($m\,d^{-1}$), W_{pco2} is the water CO_2 concentration (M), and SaW_{pco2} is the saturated water CO_2 concentration calculated at the current atmospheric CO_2 level (M).

2.2. Model Evaluation

Model parameterization for the U.S. and North America including the Mississippi River basin has been described in our previous work [*Chen et al.*, 2012; *Liu et al.*, 2013; *Tao et al.*, 2014; *Tian et al.*, 2010, 2012; *Xu et al.*, 2010; *Yang et al.*, 2014a, 2014b]. In this study, we further evaluated the DLEM simulation of water discharge and riverine C fluxes by comparing against the United States Geological Survey (USGS) water quality
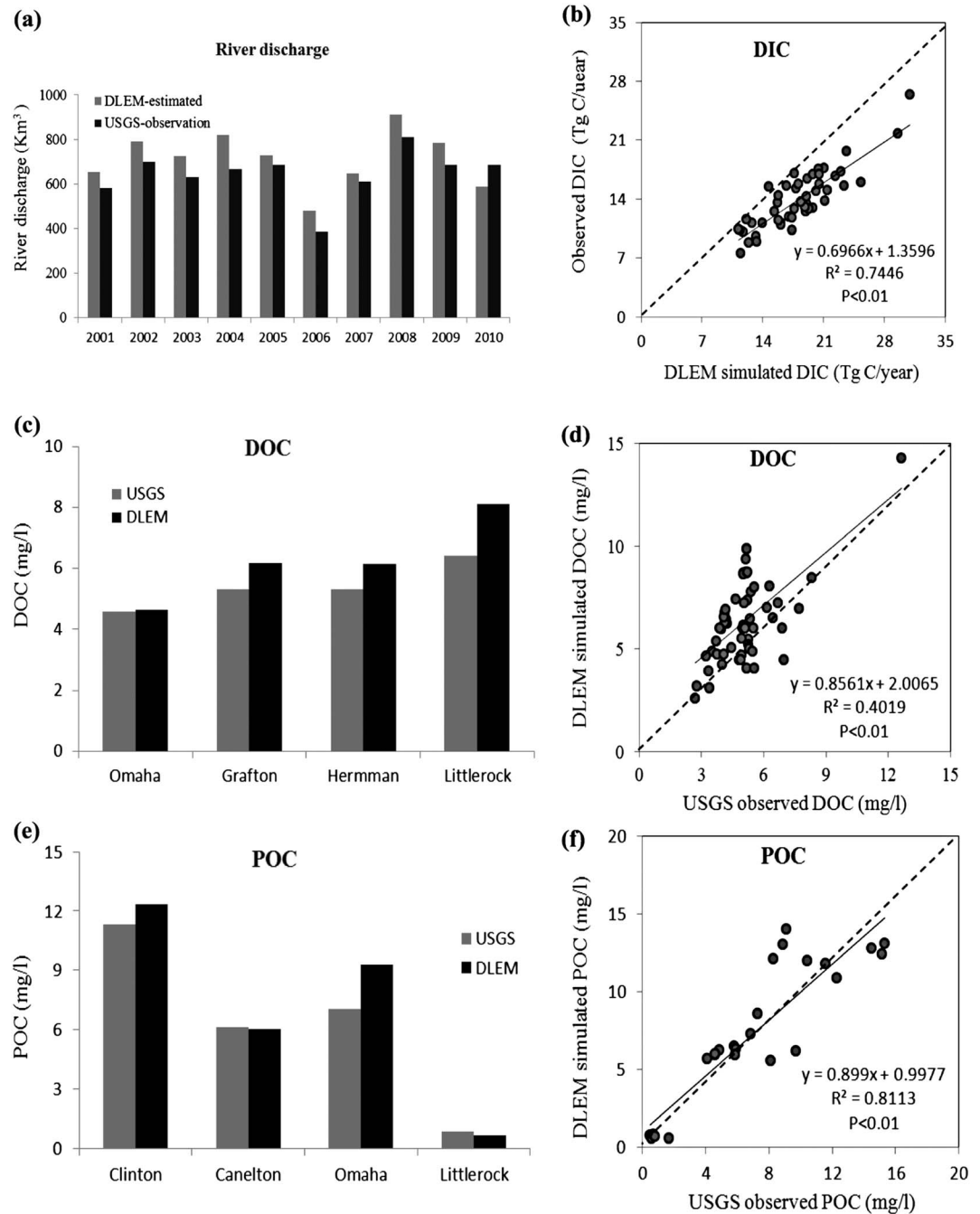
Figure 2. (a–f) Changes in the anomalies of annual precipitation (mm) and mean temperature (°C) over the Mississippi River basin during 2001–2010, relative to the 30 year average between 1961 and 1990; changes in temperature and precipitation in wet year (Figures 2c and 2d) and dry year (Figures 2e and 2f), relative to the 10 year average during 2001–2010.

data (Figure 2) for subbasins (including sites Missouri River at Omaha, Mississippi River at Grafton, Missouri River at Hermann, and Arkansas River near Little Rock) and for the entire basin. Simulated river discharge and C export (DOC, POC, and DIC) were found to be consistent with observations (Figure 2). We compared historical estimates of C export with other studies as well, which include gauging stations monitoring, empirical estimate, and process-based modeling approaches (Table 1). In general, during 1971–2000, DLEM-simulated average DIC, DOC, and total organic carbon (TOC, the sum of DOC, and TOC) export were comparable to observations from other studies such as Load Estimator (LOADEST) data [*Stets and Striegl*, 2012] and model-based estimation such

Table 1. Comparisons of Terrestrial C Export From the Mississippi River Basin Among Different Studies[a]

Chemical	Annual Flux (Tg C yr^{-1})	Period	Approach	Reference
TOC	4.61	Mean	Gauging stations monitoring	*Smith et al.* [2005]
	5.32	Mean	Empirical estimate	*Ludwig et al.* [1996]
	3.9	Mean	Physical-biological model	*Green et al.* [2006]
	4.6	1970s–2000s	LOADEST	*Stets and Striegl* [2012]
	4.1	1975–2000	Water quality model, SPARROW	*Shin et al.* [2010]
	5.7 ± 0.9	1971–2000	Process-based ecosystem model, DLEM	This study
DOC	3.08	Mean	Gauging stations monitoring	*Smith et al.* [2005]
	4.28	Mean	Empirical estimate	*Ludwig et al.* [1996]
	2.6	Mean	Process-based modeling, NEWS	*Harrison et al.* [2005]
	2.5	11970s–2000s	LOADEST	*Stets and Striegl* [2012]
	2.5	Mean	Synthesis of filed observations	*Lohrenz et al.* [2013]
	2.6 ± 0.6	1971–2000	Process-based ecosystem model, DLEM	This study
DIC	16.4	1970s–2000s	LOADEST	*Stets and Striegl* [2012]
	18. 8± 4.2	1971–2000	Process-based ecosystem model, DLEM	This study
	21	2002	Observation	*Cai et al.* [2003]
	20	2002	Water quality model, SPARROW	*Alexander et al.* [2008]
	19.5	2002	Process-based ecosystem model, DLEM	This study

[a]Note that TOC is total organic carbon, DOC is the sum of dissolved organic carbon, POC is particulate organic carbon, and DIC is dissolved inorganic carbon.

as those from SPAtially Referenced Regressions On Watershed attributes (SPARROW) model [*Shin et al.*, 2010] and the Global Nutrient Export from WaterSheds model (NEWS) [*Harrison et al.*, 2005].

2.3. Input Data

We developed gridded data sets at a spatial resolution of 5 × 5 arc min to characterize changes in environmental factors across the Mississippi River basin during 1901–2010. These gridded data include climate (i.e., mean, maximum, and minimum temperatures; precipitation; relative humidity; and solar radiation), atmospheric chemistry composition (CO_2, ozone, and nitrogen deposition), land use and cover patterns, and land management practices. The land cover/land use change data were processed as fractions of each plant functional type (i.e., forest, grassland, cropland, and urban areas) and nonvegetated cover (i.e., lake, stream, glacier, bare ground, and ocean), using multiple data sources [*Elvidge et al.*, 2007; *Klein Goldewijk and Ramankutty*, 2004; *Lehner and Doll*, 2004; *Ramankutty and Foley*, 1999]. The dominant land cover in the Mississippi River basin is cultivated cropland, accounting for approximately 52% of the area at present. The highest concentrations of cropland are in northeastern and central Iowa and southern Minnesota, where cropland makes up over 75% of the land in some counties. Land management practices mainly include irrigation [*Thenkabail et al.*, 2009], nitrogen fertilizer use (http://www.ers.usda.gov/data/fertilizeruse/), and cropping system [*Monfreda et al.*, 2008] (http://www.agcensus.usda.gov). The historical daily climate data were generated from the CRU TS 2.1 and North America Regional Reanalysis (NARR) data set [*Mesinger et al.*, 2006; *Mitchell and Jones*, 2005]. Thus, the climate data product includes information on monthly anomalies in precipitation and temperature during 1901–1980, which are from CRU, and the daily and spatial patterns during 1981–2010, which are from NARR [*Liu et al.*, 2013]. The reconstructed historical climate data (Figure 3) show that average temperature was generally higher in most years of the recent decade (2001–2010) than the long-term average between 1961 and 1990, with the highest increase of 1.3°C in 2006; annual total precipitation was lower in most years of the recent decade than the long-term average, except the year 2008 which had an increase of 85 mm relative to the mean during 1961–1990. Based on temperature and precipitation data, we calculated the Standardized Precipitation Index and defined the years 2006 and 2008 as dry and wet years, respectively, during 2001–2010. These input drivers were used to force the DLEM model to investigate the export of all carbon species (DOC, POC, and DIC) as influenced by multiple environmental changes.

2.4. Simulation Experiments and Implementation

We designed a set of simulation experiments (Table 2) to quantify the magnitude and spatial and temporal patterns of C export from the Mississippi river basin and further analyze the relative contribution of major environmental factors to changes in C export at various scales from season to century. These simulation experiments included (I) *all combined simulations*, which considered major environmental changes in climate,
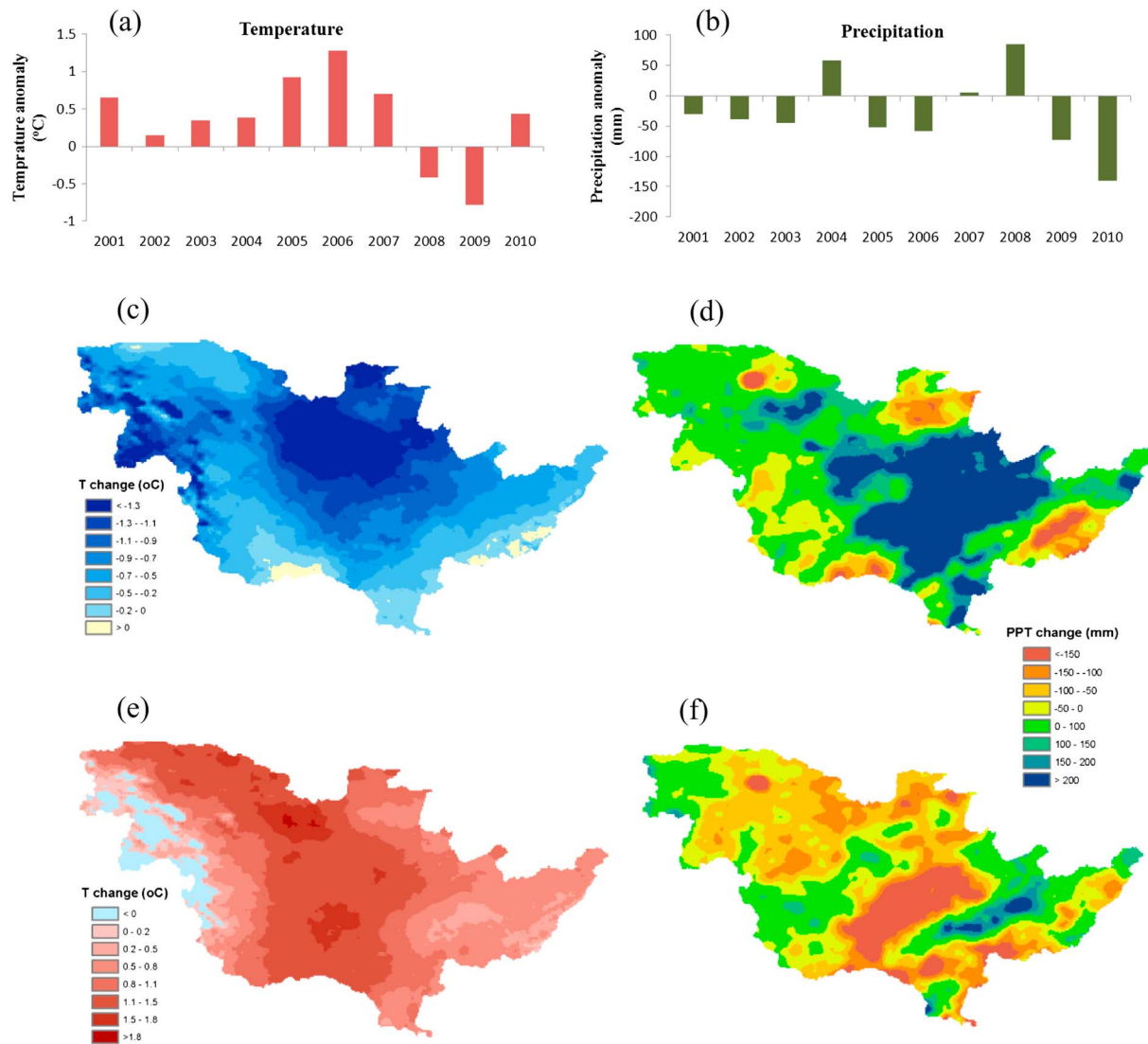
Figure 3. Comparisons of (a) DLEM-simulated water discharge (km^3 yr^{-1}), (b) total export of dissolved inorganic carbon (DIC, Tg C yr^{-1}), and (c and d) mean dissolved organic carbon concentrations (DOC, mg L^{-1}), and (e and f) particulate organic carbon concentrations (POC, mg L^{-1}), with observations over the Mississippi River basin. Note that observed DIC was derived from the published work [*Raymond and Cole*, 2003]; USGS observed DOC and POC were collected from five stations Missouri River at Omaha (site no. 6610000), Missouri River at Hermann (site no. 6934500), Mississippi River at Clinton (site no. 5420500), Mississippi River at Grafton (site no. 5587455), and Arkansas River near Little Rock (site no. 7263450).

land cover/land use change including land cover and land use change (LCLUC), and atmospheric chemical components (*ATCHM*, including CO_2, ozone, and nitrogen deposition) during 1901–2010. For attributing the relative contributions of these factors to annual variation of C export, we designed factorial simulation experiments including (II) *climate*, in which climate variables (precipitation, temperature, radiation, humidity etc.) were changed over time while other factors were held constant at 1901 levels. The same protocol was applied to simulation experiments (III) LCLUC and (IV) ATMCH to independently assess the effects of land cover/land use and atmospheric chemistry. Similarly, to determine the relative roles of precipitation and temperature on C export variations, we further conducted simulation experiments to examine the effects of precipitation (V, *PRECPT*) or temperature (VI, *T*), holding other factors constant. We also conducted a simulation experiment (VII) called *Reference*, in which all factors were held constant at 1901 levels. The *combined* and individual effects were calculated as the difference between results derived from the simulation experiment Reference and results from simulation experiments all combined, climate, LCLUC, ATMCH, PRECPT, and *T*,

Table 2. Simulation Experiments[a]

Experiments		Climate	LCLUC	CO_2	NDEP	O_3
	Equilibrium	1900	1900	1900	1900	1900
I	All combined	1901–2010	1901–2010	1901–2010	1901–2010	1901–2010
II	Climate	1901–2010	1900	1900	1900	1900
III	LCLUC	1900	1901–2010	1900	1900	1900
IV	ATMCH	1900	1900	1901–2010	1901–2010	1901–2010
V	PRECPT	1901–2010	1900	1900	1900	1900
VI	*T*	1901–2010	1900	1900	1900	1900

[a]Note that simulation experiments included all combined, in which climate, carbon dioxide (CO_2), nitrogen deposition (NDEP), ozone (O_3), land cover and land use change (LCLUC) during 2001–2010; single-factor experiments include LCLUC, climate, ATMCH (CO_2, NDEP, and O_3), precipitation (PPT), and temperature (*T*), in which only the single factor changed during 1901–2010 while other factors were kept constant in 1900(C).

respectively. Those effects represent impacts of major environmental factors on C export in the first decade of the 21st century compared to the earliest decade of the 20th century.

In this study, our analysis focuses on seasonal and interannual patterns in the recent decade (2001–2010) but all simulation experiments were conducted on a century scale during 1901–2010. In this way, we account for the legacy effects of environmental factors such as land use change and land management practices [*Tian et al.*, 2011]. The model was run at a daily time step and began with an equilibration run, which was defined as the year-to-year changes in carbon, nitrogen, and water pools in each grid less than $1\,g\,C\,m^{-2}$, $1\,mm\,H_2O$, and $1\,g\,N\,m^{-2}$, respectively. Three spin-ups with a 30 year period for each were conducted using equilibrium run conditions to reduce the biases in simulations for the transient runs. Then, the model was fed by the time series of input data set in the transient mode. More details on how the DLEM simulations are initialized and implemented have also been discussed in our previous publications [*Tian et al.*, 2012, 2015].

3. Results

3.1. Interannual Variability in the Export of DOC, POC, and DIC

From our model simulations during the 2000s, we estimated mean annual riverine exports of DOC, POC, and DIC from the Mississippi River basin of 2.6 ± 0.4 (mean ± 1 standard deviation, same hereafter) $Tg\,C\,yr^{-1}$, $3.4 \pm 0.3\,Tg\,C\,yr^{-1}$, and $18.8 \pm 3.4\,Tg\,C\,yr^{-1}$, respectively, with large interannual variations, but no statistically significant temporal trends (Figure 4). The highest C fluxes (DIC, DOC, and POC) occurred in the wet year 2008 with an increase of 32%, and the lowest fluxes were associated with the dry year 2006 with a decrease of 38% relative to the 10 year average during the 2010s. Examining the POC:DOC and DIC:DOC ratios for the period 2001–2010, we found that the POC:DOC ratio averaged 1.3 ± 0.6, with the highest ratio of 1.8 in 2006 when both POC and DOC export reached the lowest values. This was an indication that that DOC export decreased more than POC during the drought period. The DIC:DOC ratio was 7.2 ± 0.5 in the same period with a maximum ratio of 7.9 in 2008, when both DIC and DOC export climbed to the highest levels but DIC export had a higher increase than DOC. We found that the annual pattern of estimated water discharge was very similar to that of dissolved organic and inorganic C export (DIC and DOC) for the study period.
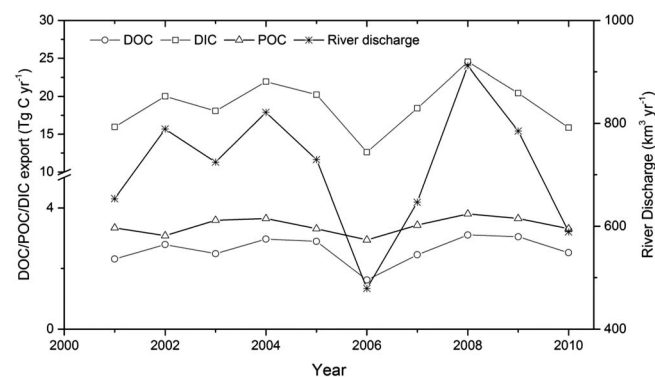
Figure 4. Annual changes in riverine fluxes of carbon species including dissolved organic carbon (DIC, $Tg\,C\,yr^{-1}$), dissolved organic carbon (DOC, $Tg\,C\,yr^{-1}$), and particulate organic carbon (POC, $Tg\,C\,yr^{-1}$) and river discharge ($km^3\,yr^{-1}$) from the Mississippi River basin during 2001–2010.

3.2. Seasonal Patterns in the Export of DOC, POC, and DIC

The largest seasonal DIC export occurred in summer (June–August), with an annual average percentage of C export over the 2001–2010 period of 32%. Maximum seasonal DOC and POC export

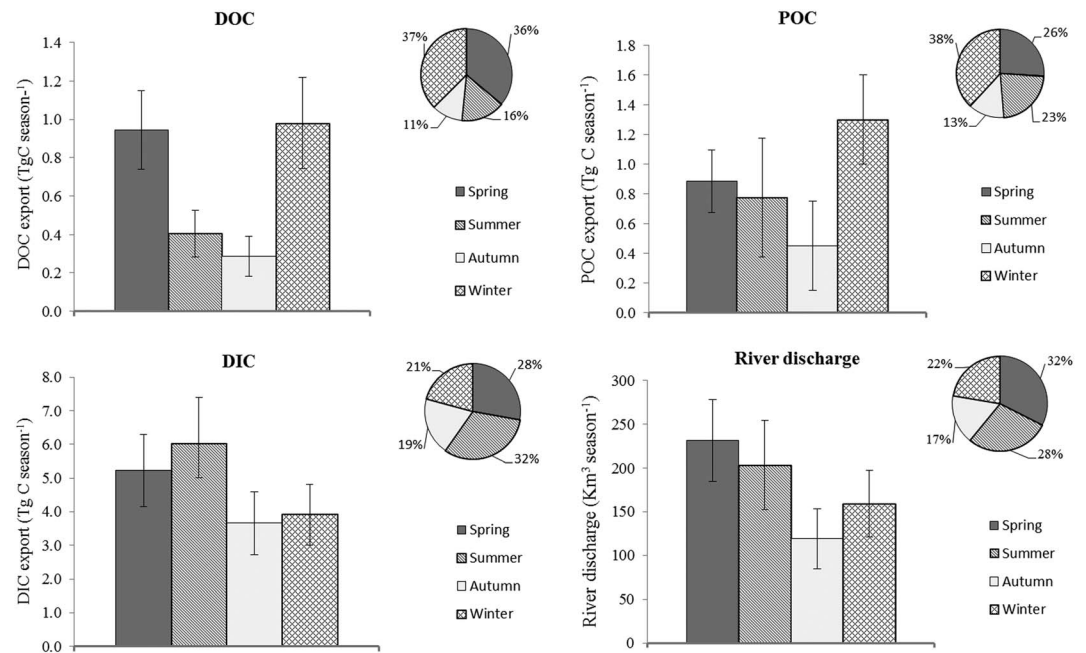**Figure 5.** Seasonal variations in dissolved organic carbon (DOC, Tg C season^{-1}), particulate organic carbon (POC, Tg C season^{-1}), dissolved inorganic carbon (DIC, Tg C season^{-1}), and river discharge (km^3 season^{-1}) across the Mississippi River basin averaged over 2001–2010. Note the spring (March–May), summer (June–August), autumn (September–November), and winter (Decameter–February).

in the model simulations were in winter (December–February), accounting for 37% and 38% of annual C export, respectively. The lowest export for all C species occurred in autumn (September–November) (Figure 5). Accordingly, the highest ratio of DIC:DOC was 14.8 in summer and the lowest was 4.0 in winter. Although the seasonal patterns of POC and DOC export were similar, POC:DOC ratios varied seasonally with the maximum ratio (1.9) in summer and the minimum (0.9) in spring, an indication of different change rates of POC and DOC export over various seasons. An analysis of seasonal patterns of water discharge found them to be similar to those of DIC export, accounting for around 30% in both spring and summer, and about 20% in both autumn and winter. Except during winter, DOC and POC export varied in a seasonal pattern consistent with that of water discharge (i.e., spring > summer > autumn). Those findings suggest that seasonal C export was related not only to changes in water discharge but also to variations in C sources across different seasons.

We further investigated how flooding events may have caused changes in C export on seasonal time scales. For example, during the June 2008 floods that affected the Midwest, the contributions expressed as percentages of the annual total rates by different C forms to summer C leaching and export increased by 9% for DOC, 9% for POC, and14% for DIC, as compared to the 10 year (2001–2010) average rates.

3.3. Spatial Distribution of DOC, POC, and DIC Exports

There were large spatial variations in C export among the subbasins of the Mississippi River basin (Figures 6a and 6b). For example, C export was greater from the relatively wet eastern parts, such as the Ohio and Tennessee Rivers subbasins, compared to the relatively dry western areas of the basin (Mississippi and Missouri basins). In the wet year (2008), both TOC and DIC export were relatively higher in most areas with a larger increase in the central Mississippi River basin (Figures 6c and 6d). In the dry year (2006), however, TOC and DIC export were slightly elevated in the northwestern parts of the Mississippi River basin while notably lower in the southeastern parts of the Mississippi River basin, particularly in the southern Mississippi River basin (Figures 6e and 6f). Spatial patterns of river discharge also varied from region to region, and the differences in wet and dry years were roughly consistent with the patterns observed for C export. We also found that DIC export had a spatial pattern very similar to that of runoff. TOC export did not closely track regional discharge patterns, suggesting other factors that contribute to the spatial and temporal variations in TOC export, such as differences in landform or land use.
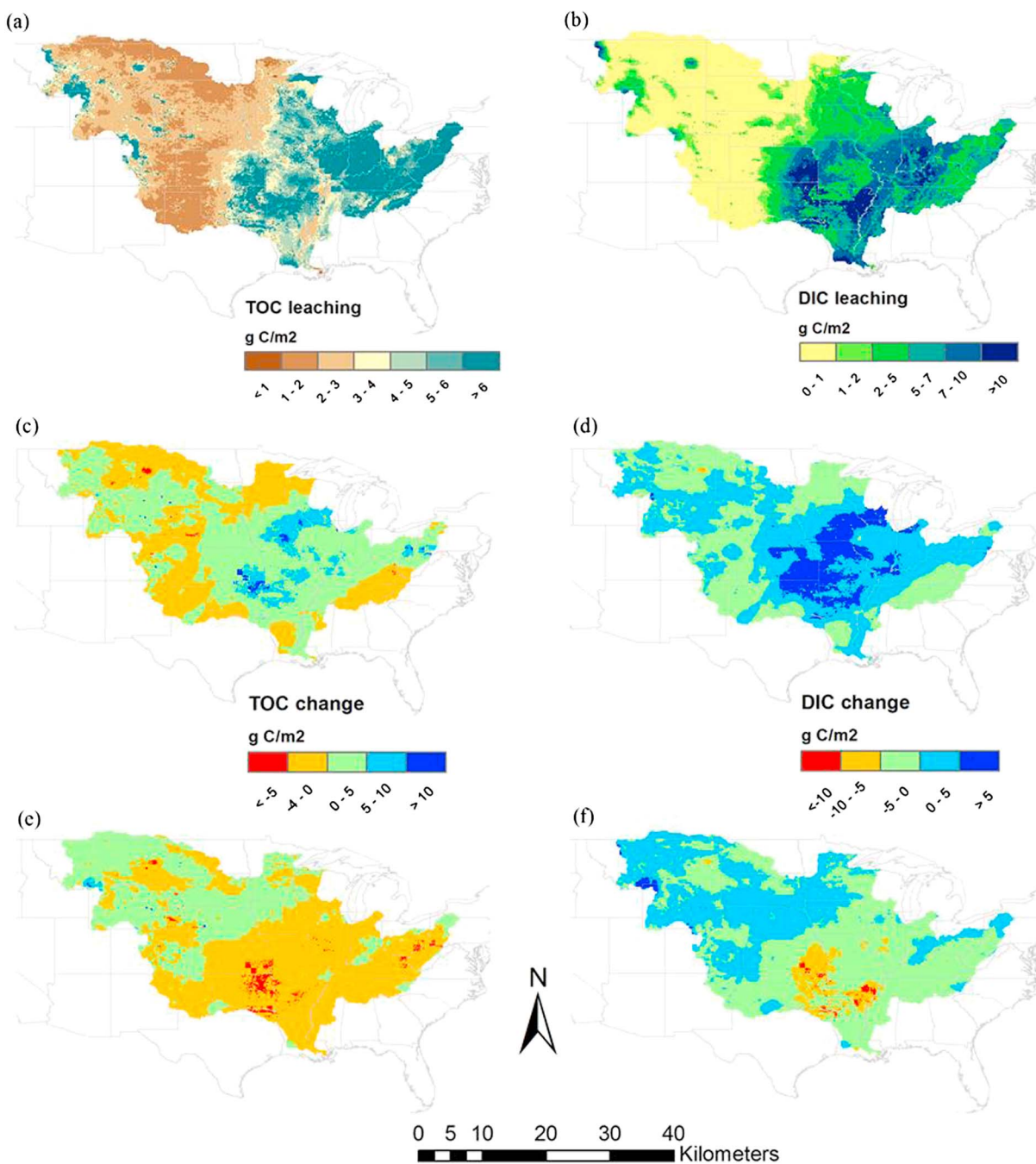
Figure 6. Spatial distributions of total organic carbon export (TOC, the sum of dissolved organic carbon and particulate organic carbon, g C m^{-2}), dissolved inorganic carbon export (DIC, g C m^{-2}), the average during 2001–2010 (a and b); and changes in (c and d) wet and (e and f) dry years relative to the 10 year average as simulated by DLEM.

3.4. Environmental Controls Over C Export

We then examined the relative importance of multiple environmental factors (e.g., climate, land use and land cover change, atmospheric CO_2, nitrogen deposition, and ozone) and their interactive effects on C export from the Mississippi river system. Three simulation experiments (climate, LCLUC, and ATMCH) were designed to quantify the relative contributions of major environmental factors to annual C export during 2001–2010 (Table 2). The results support the view that land management (LCLUC) consistently had the largest impact on annual C export, followed by atmospheric chemistry (ATMCH), when comparing the first decade of the
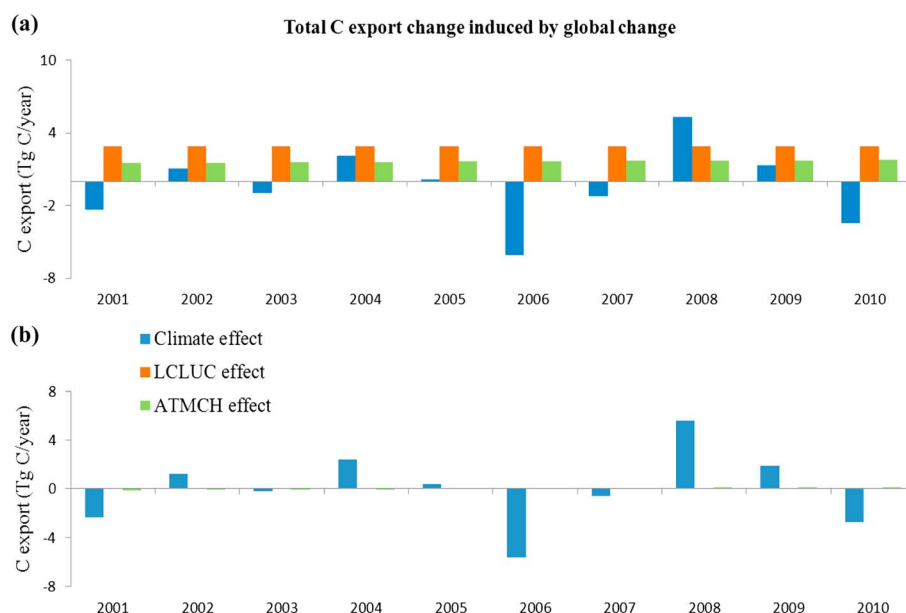
(a)

(b)

Figure 7. (a) Relative contributions of environmental factors to total carbon export over the Mississippi River basin during 2001–2010, compared to the reference (the first decade of the 20th century); and (b) the anomaly of each environmental factor relative to the 10 year average in the 2000s.

21st century to the first decade of the 20th century. However, temperature and precipitation were the dominant factors shaping the year-to-year patterns of C export (Figure 7), on average accounting for more than 55%, 50%, and 80% of the interannual variations in DOC, POC, and DIC export, respectively.

To further explore the relative effects of temperature and precipitation on C export, we conducted two additional simulations, one in which precipitation was allowed to vary while others were kept unchanged (*PRECIP*) and the other in which temperature (*T*) was allowed to vary while other factors were kept constant. In general, annual variations in river discharge and C export were mainly determined by annual precipitation variations, implying that heavy rainfall events induced changes in river discharge that in turn largely influenced C fluxes from land to ocean.

4. Discussion

4.1. Modeling Carbon Dynamics in the Land-Aquatic-Ocean Interfaces

There has been considerable effort to understand the mechanisms controlling organic and inorganic terrestrial C export from the major river basins of the world. For the Mississippi River basin, two approaches have generally been taken—(1) an empirical, correlative approach using statistics to analyze trends and relations to potentially controlling variables [e.g., *Cai* 2003; *Donner et al.*, 2004; *Lohrenz et al.*, 1999; *Raymond and Cole*, 2003; *Raymond et al.*, 2008] and (2) mechanistic models. Most models, however, have either used coarse spatial scales or have been overly simplistic with the potentially important controlling environmental factors and this has limited their predictive capability. Consequently, the relative roles of controlling factors, both individually and in combination with each other, has been difficult to discern. The approach applied in this study provides an enhanced understanding of hydrologic-biogeochemical processes associated with the movement of water and C through terrestrial reservoirs and the river network to the ocean under climate and anthropogenic forcing. The level of detail incorporated into DLEM 2.0 enables us to examine how several rapidly changing environmental factors including climate (temperature and precipitation), land use, atmospheric CO_2, and nitrogen deposition have affected C export from land to ocean. This is a major advance because it has not only enabled us to discern the relative importance of various anthropogenic changes on terrestrial, riverine, and ocean systems, but it will enable us to predict the effects of future changes in our climate. In a separate effort we are linking the DLEM with a coastal ocean coupled hydrodynamic-biogeochemical model with the goal of understanding how changes on land will affect ocean productivity and biogeochemical cycling.

4.2. Estimation of C Export in the Mississippi River Basin and Comparison to Previous Studies

DLEM-simulated export of all forms of C agreed well with both empirical and other model-based estimates for the recent past. For TOC, the DLEM-estimated average flux for the last three decades of the 20th century (5.7 ± 0.9 Tg C yr^{-1}) is similar to the empirical results of Ludwig et al. (5.32 Tg C yr^{-1}) [*Ludwig et al.*, 1996], but slightly higher than other estimates that range from 3.9 Tg C yr^{-1} to 4.61 Tg C yr^{-1} [*Green et al.*, 2006; *Shin et al.*, 2010; *Smith et al.*, 2005; *Stets and Striegl*, 2012]. We found large interannual variability in TOC export, with deviations from the 10 year (2001–2010) average of approximately +30% to −38% in climate extreme years. In light of this high variability, offsets in the periods when empirical studies were conducted relative to the 30 year average estimate of the DLEM may partially explain our higher estimate of TOC export. The average DOC export estimated by DLEM was 2.6 ± 0.6 Tg C yr^{-1}, which is comparable to model-based estimates of 2.6 Tg C yr^{-1} and 2.5 Tg C yr^{-1} from NEWS [*Harrison et al.*, 2005] and LOADEST [*Stets and Striegl*, 2012], respectively, and also comparable to an empirical mean of 2.5 Tg C yr^{-1} based on a synthesis of field observations [*Lohrenz et al.*, 2013]. The greatest amount of C is exported from the Mississippi River basin in the form of DIC. The simulated DIC export was 19.5 Tg C in 2002, which is very close to the SPARROW model-simulated DIC export of 20 Tg C [*Alexander et al.*, 2008] and the empirically observed DIC export of 21 Tg C [*Cai*, 2003; *Lohrenz et al.*, 2013]. We find good agreement even with longer-term estimates of export. For example, for the 1971–2000 interval, the DLEM-estimate of DIC export was within 5% of the LOADEST estimation of 16.4 Tg C yr^{-1} [*Stets and Striegl*, 2012], after correcting for a 10% difference in drainage basin size. The agreement between the DLEM, other models, and empirical measures of the various forms of C export from the Mississippi River Basin over different periods of time is encouraging, because it lends support for the validity of our mechanistic understanding of the various factors that contribute to the timing, magnitude, and form of C export. The model appears to provide a reasonable representation of interactive effects of land cover, land use and management, and climate on both the hydrology and C biogeochemistry of a climatically, geologically, and biogeographically diverse major watershed of the world.

4.3. Long-Term and Short-Term Controls on C Export

By hindcasting C dynamics and export in the Mississippi River basin for the past 110 years, we have developed a mechanistic understanding of the relative importance of land use change and management practices as well as various aspects of climate variability and change on controlling trends and variability in C export. Our simulations attribute a substantial fraction of increased C export over the past century to land use change and management practices. Human activity has greatly modified the land cover and climate of the Earth, which has altered the water balance, and biogeochemistry of the terrestrial biosphere and weathering of the land surface [*Regnier et al.*, 2013]. Consistent with our results, previous studies contend that on a centurial scale over the Mississippi River basin, the increase in historical DIC export has been mainly due to direct anthropogenic drivers, i.e., land cover/land use change and intensive land management practices [*Raymond and Cole*, 2003; *Raymond et al.*, 2008].

The major effect of climate on C export in the Mississippi has been on seasonal and annual variability in C export. Of the climate variables considered, temperature and precipitation accounted for the largest portion of the total variation in organic and inorganic C export. Between 2001 and 2010, precipitation and temperature had the largest influence on the magnitude and year-to-year variability of river discharge, a major driver mediating export of all C species in the DLEM model. While concentrations of different forms of C varied over time, discharge varied to a far greater extent, which explains its primary importance in controlling variability in C export. We found that annual variations in precipitation shaped the spatial and temporal patterns of surface runoff, streamflow, and river discharge. We also found that temperature and precipitation influenced sources of C export by partially regulating plant growth, litter fall, soil moisture, decomposition of organic matter, and root respiration. The importance of these factors has been reported from field studies as well [*Billett et al.*, 2007; *Johnson et al.*, 1997; *Köhler et al.*, 2002]. In simulations to explore the effect of elevated temperatures (in which only the temperature factor was allowed to vary), we noted an enhancement of soil respiration, which leads to greater leachate production and DOC availability for C export. While temperature affected the form and availability of C for export, the magnitude of C export was closely linked to river discharge. The interplay between temperature and precipitation is exemplified by comparing an extreme wet and cold year to an extreme dry but warm year. For the wet and cold year, increased discharge and C export occurred, even though low temperatures reduced the production and availability of organic leachate. The dry

and warm year resulted in maximum observed decreases in river discharge and C export, even though high temperatures favored DOC leachate production and availability. These findings are supported by recent field studies [*Bianchi et al.*, 2013; *Dhillon and Inamdar*, 2013]. Comparison of seasonal patterns provides additional evidence for a combined effect of changing precipitation and temperature on sources of C export and river discharge. This can be illustrated by considering the differing effects of temperature and precipitation for DIC. The flooding season is typically in spring while the maximum DIC export season is in summer. This is because higher temperatures in summer stimulate soil respiration thereby resulting in increased availability of DIC for export. Previous studies have shown how climate change can alter the surface hydrologic cycle, including timing, frequency, and magnitude of hydrologic flows [*Huntington*, 2006; *Oki and Kanae*, 2006], and our simulations provide evidence that these changing patterns are likely to have consequences for C export.

4.4. Uncertainty and Future Research Needs

This is the first study to report on the export of all forms of C from a major river basin using a mechanistic model that provides an understanding of the relative importance of the major climatic and land use change factors controlling short- and long-term trends and variability in C export. While our results agree well with other empirical and modeling studies, we also acknowledge that our model does not yet account for several important factors that are known to influence material export from river systems, both locally and regionally. We have greatly simplified land management practices omitting any consideration of agronomic practices (e.g., manure application) and natural disturbances (e.g., pest outbreaks and fire). Nor have we included factors such as effects of human infrastructure on rivers (e.g., dams), which are known to have reduced sediment export from the Mississippi River substantially since the turn of the last century [*Meade and Moody*, 2010]. These factors do affect C export through changing the physical environment, and altering the variation and cycles of river flow that occur daily, seasonally, and interannually, and thus have enormous biological consequences. We also assumed that landscape and river network characteristics (e.g., upper Mississippi and low head dams) remain relatively stable at annual and decadal time scales. This assumption does not include the pre-2001 legacy effect of past impounds, which may bring uncertainty to our estimation of C export over the most recent decade [*Walling*, 2006]. Finally, we have ignored all aspects of in-stream metabolism, including the processing of terrestrial organic matter and contributions of often-time high-quality autochthonous organic C that can be exported to the sea [*Green et al.*, 2006; *Shin et al.*, 2010]. We are currently refining the DLEM to explicitly account for these limitations of the current version, focusing initially on in-stream metabolism, natural disturbance, and dams.

5. Conclusions

We have taken a drainage basin approach to understand the effects of climatic and anthropogenic changes on the hydrologically coupled terrestrial system, the Mississippi River basin of North America that drains to the Gulf of Mexico. Our mechanistic approach using the DLEM 2.0 model enables us to discern the relative effects of different aspects of climate and land use change, individually and in combination with each other, on organic and inorganic C export. Such an approach is unprecedented and points to major effects of climate-related factors on the magnitude and seasonal and interannual variations of C export from a large river system. The findings derived from this study have profound implications for the carbon cycle and ecosystem dynamics not only for the terrestrial regime but for inland and coastal aquatic regimes as well, given that different species of carbon will undergo differential biogeochemical processing and, consequently, will experience different fates. Our study further shows the interrelated effects of temperature and precipitation on the timing and magnitude of export of the various forms of C. Aside from an overall warming, expectations for the future climate in North America include increased variability, with increased severity of storms, more intense rainfalls, and prolonged periods of drought, all of which are likely to have a major impact on riverine fluxes and hence on ecosystem and biogeochemical processes in the coastal ocean.

Models such as this will be indispensable for helping to develop scientifically defensible strategies to manage C and nutrients, water availability, and coastal ocean productivity. While this study has focused on the Mississippi River basin as a model system, the approach can be applied to other watersheds with a variety of land uses and covers. The knowledge and understanding provided by such an approach will be essential for both predicting and managing change in the C cycle at land-aquatic-ocean interfaces.

References

Allen, R. G., L. S. Pereira, D. Raes, and M. Smith (1998), *Crop Evapotranspiration: Guidelines for Computing Crop Water Requirements*, *FAO Irrigation and Drainage Pap.*, 300 pp., Rome.

Alexander, R. B., R. A. Smith, G. E. Schwarz, E. W. Boyer, J. V. Nolan, and J. W. Brakebill (2008), Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin, *Environ. Sci. Technol.*, *42*(3), 822–830.

Bauer, J. E., W. J. Cai, P. A. Raymond, T. S. Bianchi, C. S. Hopkinson, and P. A. G. Regnier (2013), The changing carbon cycle of the coastal ocean, *Nature*, *504*(7478), 61–70.

Belmans, C., J. G. Wesseling and R. A. Feddes (1983), Simulation-model of the water balance of a cropped soil: SWATRE, *J. Hydrol.*, *63*(3–4), 271–286.

Bianchi, T. S., et al. (2013), Enhanced transfer of terrestrially derived carbon to the atmosphere in a flooding event, *Geophys. Res. Lett.*, *40*, 116–122, doi:10.1029/2012GL054145.

Billett, M. F., M. H. Garnett, and F. Harvey (2007), UK peatland streams release old carbon dioxide to the atmosphere and young dissolved organic carbon to rivers, *Geophys. Res. Lett.*, *34*, L23401, doi:10.1029/2007GL031797.

Butman, D., and P. A. Raymond (2011), Significant efflux of carbon dioxide from streams and rivers in the United States, *Nat. Geosci.*, *4*(12), 839–842.

Cai, W. J. (2003), Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume, *Geophys. Res. Lett.*, *30*(2), 1032, doi:10.1029/2002GL016312.

Cai, W. J. (2011), Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, *Annu. Rev. Mar. Sci.*, *3*, 123–145.

Cai, W. J., Z. H. A. Wang, and Y. C. Wang (2003), The role of marsh-dominated heterotrophic continental margins in transport of CO_2 between the atmosphere, the land-sea interface and the ocean, *Geophys. Res. Lett.*, *30*(16), doi:10.1029/2003GL017633.

Chantigny, M. H. (2003), Dissolved and water-extractable organic matter in soils: A review on the influence of land use and management practices, *Geoderma*, *113*(3–4), 357–380.

Chaubey, I., D. Sahoo, B. E. Haggard, A. D. Matlock, and T. A. Costello (2007), Nutrient retention, nutrient limitation, and sediment-nutrient interactions in a pasture-dominated stream, *Trans. ASABE*, *50*(1), 35–44.

Chen, G., H. Q. Tian, C. Zhang, M. L. Liu, W. Ren, W. Q. Zhu, A. Chappelka, S. A. Prior, and G. B. Lockaby (2012), Drought in the Southern United States over the 20th century: Variability and its impacts on terrestrial ecosystem productivity and carbon storage, *Clim. Change*, *114*(2), 379–397.

Chen, H., H. Q. Tian, M. L. Liu, J. Melillo, S. F. Pan, and C. Zhang (2006), Effect of land-cover change on terrestrial carbon dynamics in the southern United States, *J. Environ. Qual.*, *35*(4), 1533–1547.

Chen, J. M., X. Y. Chen, W. M. Ju, and X. Y. Geng (2005), Distributed hydrological model for mapping evapotranspiration using remote sensing inputs, *J. Hydrol.*, *305*(1–4), 15–39.

Coe, M. T. (2000), Modeling terrestrial hydrological systems at the continental scale: Testing the accuracy of an atmospheric GCM, *J. Clim.*, *13*(4), 686–704.

Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, *10*(1), 171–184.

Dhillon, G. S., and S. Inamdar (2013), Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering uncharted waters?, *Geophys. Res. Lett.*, *40*, 1322–1327, doi:10.1002/grl.50306.

Donner, S. D., C. J. Kucharik, and J. A. Foley (2004), Impact of changing land use practices on nitrate export by the Mississippi River, *Global Biogeochem. Cycles*, *18*, GB1028, doi:10.1029/2003GB002093.

Elvidge, C. D., B. T. Tuttle, P. S. Sutton, K. E. Baugh, A. T. Howard, C. Milesi, B. L. Bhaduri, and R. Nemani (2007), Global distribution and density of constructed impervious surfaces, *Sensors-Basel*, *7*(9), 1962–1979.

Findlay, S. (2010), Stream microbial ecology, *J. North Am. Benthological Soc.*, *29*(1), 170–181.

Foley, J. A., C. J. Kucharik, T. E. Twine, M. T. Coe, and S. D. Donner (2004), Land use, land cover, and climate change across the Mississippi Basin: Impacts on selected land and water resources, in *Ecosystems and Land Use Change*, edited by R. S. Defries, G. P. Asner, and R. A. Houghton, pp. 249–261, AGU, Washington, D. C.

Green, R., T. Bianchi, M. Dagg, N. Walker, and G. Breed (2006), An organic carbon budget for the Mississippi River turbidity plume and plume contributions to air-sea CO_2 fluxes and bottom water hypoxia, *Estuaries Coasts*, *29*(4), 579–597.

Guérin, F., G. Abril, D. Serca, C. Delon, S. Richard, R. Delmas, A. Tremblay, and L. Varfalvy (2007), Gas transfer velocities of CO_2 and CH_4 in a tropical reservoir and its river downstream, *J. Mar. Syst.*, *51*(1–4), 161–172.

Harrison, J. A., N. Caraco, and S. P. Seitzinger (2005), Global patterns and sources of dissolved organic matter export to the coastal zone: Results from a spatially explicit, global model, *Global Biogeochem. Cycles*, *19*, GB4S04, doi:10.1029/2005GB002480.

Holford, I. C. R., and G. E. G. Mattingly (1975), Surface-areas of calcium-carbonate in soils, *Geoderma*, *13*(3), 247–255.

Huntington, T. G. (2006), Evidence for intensification of the global water cycle: Review and synthesis, *J. Hydrol.*, *319*(1–4), 83–95.

Jarvis, P. G., and J. I. L. Morison (1981), Stomatal control of transpiration and photosynthesis, in *Stomatal Physiology*, edited by P. G. Jarvis and T. A. Mansfield, pp. 247–279, Cambridge Univ. Press, New York.

Johnson, L., C. Richards, G. Host, and J. Arthur (1997), Landscape influences on water chemistry in Midwestern stream ecosystems, *Freshwater Biol.*, *37*(1), 193–208.

Klein Goldewijk, K., and N. Ramankutty (2004), Land cover change over the last three centuries due to human activities: The availability of new global data sets, *GeoJournal*, *61*, 335–344.

Köhler, S., I. Buffam, A. Jonsson, and K. Bishop (2002), Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden, *Aquat. Sci.*, *64*(3), 269–281.

Lehner, B., and P. Doll (2004), Development and validation of a global database of lakes, reservoirs and wetlands, *J. Hydrol.*, *296*(1–4), 1–22.

Liu, M., H. Tian, Q. Yang, J. Yang, X. Song, S. E. Lohrenz, and W.-J. Cai (2013), Long-term trends in evapotranspiration and runoff over the drainage basins of the Gulf of Mexico during 1901–2008, *Water Resour. Res.*, *49*, 1988–2012, doi:10.1002/wrcr.20180.

Lohrenz, S. E., G. L. Fahnenstiel, D. G. Redalje, G. A. Lang, X. G. Chen, and M. J. Dagg (1997), Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River, *Mar. Ecol. Prog. Ser.*, *155*, 45–54.

Lohrenz, S. E., G. L. Fahnenstiel, D. G. Redalje, G. A. Lang, M. J. Dagg, T. E. Whitledge, and Q. Dortch (1999), Nutrients, irradiance, and mixing as factors regulating primary production in coastal waters impacted by the Mississippi River plume, *Cont. Shelf Res.*, *19*(9), 1113–1141.

Lohrenz, S. E., W. J. Cai, S. Chakraborty, K. Gundersen, and M. C. Murrell (2013), Nutrient and carbon dynamics in a large river-dominated coastal ecosystem: The Mississippi-Atchafalaya River system, in *Biogeochemical Dynamics at Major River-Coastal Interfaces*, edited by T. S. Bianchi, M. A. Allison, and W.-J. Cai, pp. 448–472, Cambridge Univ. Press, New York.

Ludwig, W., J. L. Probst, and S. Kempe (1996), Predicting the oceanic input of organic carbon by continental erosion, *Global Biogeochem. Cycles*, *10*(1), 23–41, doi:10.1029/95GB02925.

Mackenzie, F. T., L. M. Ver, and A. Lerman (2000), Coastal-zone biogeochemical dynamics under global warming (vol 42, pg 193, 2000), *Int. Geol. Rev.*, *42*(12), 1148–1149.

Meade, R. H., and J. A. Moody (2010), Causes for the decline of suspended-sediment discharge in the Mississippi River system, 1940–2007, *Hydrol. Process*, *24*(1), 35–49.

Merritt, W. S., R. A. Letcher, and A. J. Jakeman (2003), A review of erosion and sediment transport models, *Environ. Modell. Software*, *18*(8–9), 761–799.

Mesinger, F., et al. (2006), North American regional reanalysis, *Bull. Am. Meteorol. Soc.*, *87*(3), 343–360.

Mitchell, T. D., and P. D. Jones (2005), An improved method of constructing a database of monthly climate observations and associated high-resolution grids, *Int. J. Climatol.*, *25*(6), 693–712.

Monfreda, C., N. Ramankutty and J. A. Foley (2008), Farming the planet: 2. Geographic distribution of crop areas, yields, physiological types, and net primary production in the year 2000, *Global Biogeochem. Cycles*, *22*(1), doi:10.1029/2007GB002947.

Oki, T., and S. Kanae (2006), Global hydrological cycles and world water resources, *Science*, *313*(5790), 1068–1072.

Plummer, L. N., T. M. L. Wigley, and D. L. Parkhurst (1978), Kinetics of calcite dissolution in CO_2-water systems at 5-degrees-C to 60-degrees-C and 0.0 to 1.0 atm CO_2, *Am. J. Sci.*, *278*(2), 179–216.

Rabalais, N. N., R. E. Turner, and W. J. Wiseman (2002), Gulf of Mexico hypoxia, aka "The dead zone", *Annu. Rev. Ecol. Syst.*, *33*, 235–263.

Ramankutty, N., and J. A. Foley (1999), Estimating historical changes in global land cover: Croplands from 1700 to 1992, *Global Biogeochem. Cycles*, *13*(4), 997–1027.

Raymond, P. A., and J. J. Cole (2003), Increase in the export of alkalinity from North America's largest river, *Science*, *301*(5629), 88–91.

Raymond, P. A., N. H. Oh, R. E. Turner, and W. Broussard (2008), Anthropogenically enhanced fluxes of water and carbon from the Mississippi River, *Nature*, *451*(7177), 449–452.

Raymond, P. A., et al. (2013), Global carbon dioxide emissions from inland waters, *Nature*, *503*(7476), 355–359.

Regnier, P., R. Wollast, and C. I. Steefel (1997), Long-term fluxes of reactive species in macrotidal estuaries: Estimates from a fully transient, multicomponent reaction-transport model, *Mar. Chem.*, *58*(1–4), 127–145.

Regnier, P., et al. (2013), Anthropogenic perturbation of the carbon fluxes from land to ocean, *Nat. Geosci.*, *6*, 597–607, doi:10.1038/ngeo1830.

Ren, W., H. Tian, B. Tao, J. Yang, S. Pan, W. Cai, S. Lohrenz, R. He, and C. S. Hopkinson (2015), Large increase in dissolved inorganic carbon flux from the Mississippi River to Gulf of Mexico due to climatic and anthropogenic changes over the 21st century, *J. Geophys. Res. Biogeosci.*, *120*, 724–736, doi:10.1002/2014JG002761.

Running, S. W., and J. C. Coughlan (1988), A General-model of forest ecosystem processes for egionalapplications. 1. Hydrologic balance, canopy gas-exchange and primary production processes, *Ecol. Model.*, *42*(2), 125–154.

Schilling, K. E., K. S. Chan, H. Liu, and Y. K. Zhang (2010), Quantifying the effect of land use land cover change on increasing discharge in the Upper Mississippi River, *J. Hydrol.*, *387*(3-4), 343–345.

Shin, Y.-J., M. Travers, and O. Maury (2010), Coupling low and high trophic levels models: Towards a pathways-orientated approach for end-to-end models, *Prog. Oceanogr.*, *84*(1–2), 105–112.

Smith, S. V., R. O. Sleezer, W. H. Renwick, and R. W. Buddemeier (2005), Fates of eroded soil organic carbon: Mississippi basin case study, *Ecol. Appl.*, *15*(6), 1929–1940.

Stets, E. G., and R. G. Striegl (2012), Carbon export by rivers draining the conterminous United States, *Inland Waters*, *2*(4), 177–184.

Tank, J. L., E. J. Rosi-Marshall, N. A. Griffiths, S. A. Entrekin, and M. L. Stephen (2010), A review of allochthonous organic matter dynamics and metabolism in streams, *J. North Am. Benthological Soc.*, *29*(1), 118–146.

Tao, B., H. Q. Tian, W. Ren, J. Yang, Q. C. Yang, R. Y. He, W. J. Cai, and S. Lohrenz (2014), Increasing Mississippi river discharge throughout the 21st century influenced by changes in climate, land use, and atmospheric CO_2, *Geophys. Res. Lett.*, *41*, 4978–4986, doi:10.1002/2014GL060361.

Thenkabail, P. S., et al. (2009), Global irrigated area map (GIAM), derived from remote sensing, for the end of the last millennium, *Int. J. Remote Sens.*, *30*(14), 3679–3733.

Tian, H., Q. Yang, R. Najjar, W. Ren, M. A. M. Friedrichs, C. S. Hopkinson, and S. Pan (2015), Anthropogenic and climatic influences on carbon fluxes from eastern North America to the Atlantic Ocean: A process-based modeling study, *J. Geophys. Res. Biogeosci.*, *120*, 757–772, doi:10.1002/2014JG002760.

Tian, H. Q., G. S. Chen, M. L. Liu, C. Zhang, G. Sun, C. Q. Lu, X. F. Xu, W. Ren, S. F. Pan, and A. Chappelka (2010), Model estimates of net primary productivity, evapotranspiration, and water use efficiency in the terrestrial ecosystems of the southern United States during 1895–2007, *For. Ecol. Manage.*, *259*(7), 1311–1327.

Tian, H. Q., et al. (2011), China's terrestrial carbon balance: Contributions from multiple global change factors, *Global Biogeochem. Cycles*, *25*, doi:10.1029/2010GB003838.

Tian, H. Q., et al. (2012), Century-scale responses of ecosystem carbon storage and flux to multiple environmental changes in the southern United States, *Ecosystems*, *15*(4), 674–694.

Tian, H. Q., G. Chen, C. Lu, X. Xu, D. Hayes, W. Ren, S. Pan, D. Huntzinger, and S. Wofsy (2014), North American terrestrial CO_2 uptake largely offset by CH_4 and N_2O emissions: Toward a full accounting of the greenhouse gas budget, *Clim. Change*, *129*, 413–426.

Walling, D. E. (2006), Human impact on land-ocean sediment transfer by the world's rivers, *Geomorphology*, *79*(3–4), 192–216.

Wigmosta, M. S., L. W. Vail, and D. P. Lettenmaier (1994), A distributed hydrology-vegetation model for complex terrain, *Water Resour. Res.*, *30*(6), 1665–1679.

Williams, J. R., and H. D. Berndt (1977), Sediment yield prediction based on watershed hydrology, *Trans. ASAE*, *20*(6), 1100–1104.

Xu, X. F., H. Q. Tian, C. Zhang, M. L. Liu, W. Ren, G. S. Chen, C. Q. Lu, and L. Bruhwiler (2010), Attribution of spatial and temporal variations in terrestrial methane flux over North America, *Biogeosciences*, *7*(11), 3637–3655.

Yang, Q., H. Tian, M. A. M. Friedrichs, M. Liu, X. Li, and J. Yang (2014a), Hydrological responses to climate and land-use changes along the North American east coast: A 110-year historical reconstruction, *J. Am. Water Resour. Assoc.*, doi:10.1111/jawr.12232.

Yang, Q., et al. (2014b), Spatiotemporal patterns of evapotranspiration along the North American east coast as influenced by multiple environmental changes, *Ecohydrology*, doi:10.1002/eco.1538.

Yang, Q. C., H. Q. Tian, M. A. M. Friedrichs, C. S. Hopkinson, C. Q. Lu, and R. G. Najjar (2015), Increased nitrogen export from eastern North America to the Atlantic Ocean due to climatic and anthropogenic changes during 1901–2008, *J. Geophys. Res. Biogeosci.*, *120*(6), 1046–1068.